

## \* NOTICES \*

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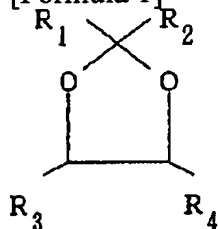
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2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## CLAIMS

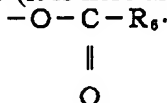
[Claim(s)]

[Claim 1] a) 1 - 40% of c 1 - 25% of insidious photo-oxide, and 10 - 40% [ of b film formation polymers ] organic additives with the following structure expression, and d -- the positive type photoresist constituent which consists of mixture of a suitable solvent.

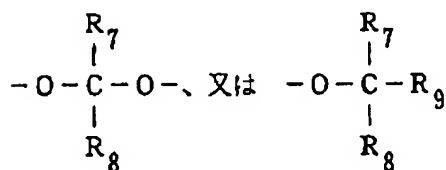
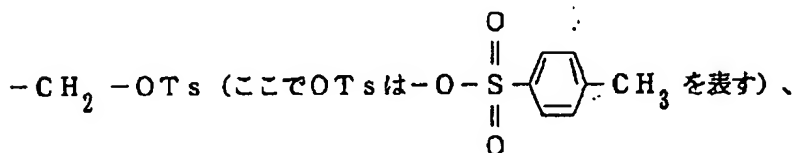
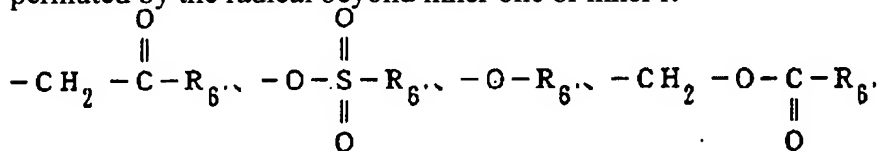
[Formula 1]



R1 is phenyl, permutation phenyl, or alkyl (CN H2N+1 and N). And R2 desirable -- 1, 2, or 3 -- expressing -- R3 And R4 alkyl (CN H2N+1), the cycloalkyl which has ten carbon atoms from four pieces preferably, -CN, -NO2, a halogen atom, -CX3 (it is here and X expresses a halogen atom), -SO3-R5, and here -- R5 -- H, -CX3, and -PO3 -- or



Here, it is R6. Alkyl (CN H2N+1) phenyl, naphthyl, anthryl or R3, R4, and R5 [Formula 2] showing the anthryl permuted by the radical beyond inner one or inner it



Here, it is R7 and R8. And R9 R3, R4, or R5 [Claim 2] which may be one of radicals The photoresist constituent according to claim 1 whose insidious photo-oxide is iodonium salt or sulfonium salt.

[Claim 3] The photoresist constituent according to claim 1 whose insidious photo-oxide is a phenyliodonium salt or phenyl sulfonium salt.

[Claim 4] The photoresist constituent according to claim 1 whose film formation polymer is an imide polymer or a hydroxystyrene polymer.

[Claim 5] The photoresist constituent according to claim 1 whose film formation polymer is polyimide with which about 5 to about 98% of the imide radical is blocked by the acid permutation active group.

[Claim 6] The photoresist constituent according to claim 5 whose film formation polymer is Pori (maleimide-course CHIREN).

[Claim 7] The photoresist constituent according to claim 1 whose film formation polymer is a hydroxystyrene polymer by which about 5 to about 98% of the hydroxystyrene radical is blocked by the acid permutation active group.

[Claim 8] The photoresist constituent according to claim 7 whose film formation polymer is Pori (hydroxystyrene) or Pori (hydroxystyrene-2 sulfur oxide).

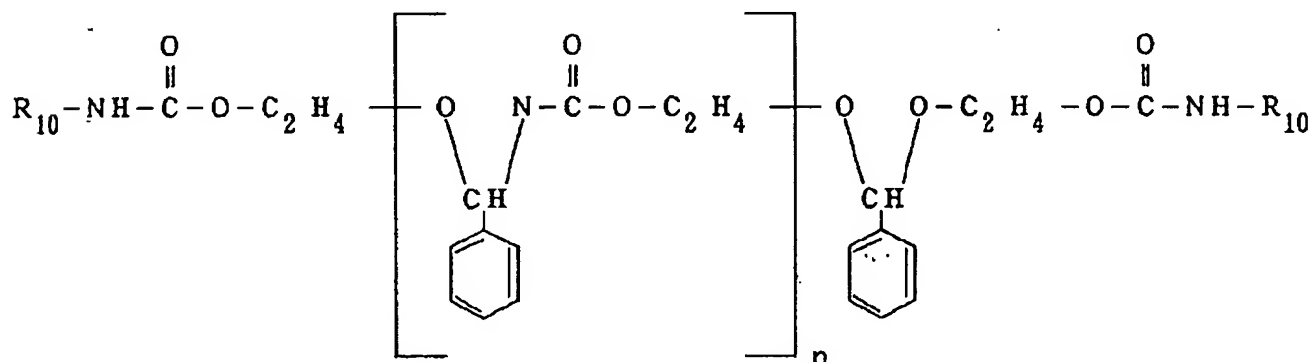
[Claim 9] The photoresist constituent according to claim 9 whose acid permutation active group is an oxy-carbonyl group.

[Claim 10] The photoresist constituent according to claim 7 whose acid permutation active group is a t-butoxycarbonyl group.

[Claim 11] The photoresist constituent according to claim 1 whose organic additive is an acetal or ketal.

[Claim 12] An organic additive 1, the 4-G O-tosyl -2, a 3-O-isopropylidene-L-sleigh toll, An oligo acetal, a diacetone-D-glucose, 3-O-acetyl-6-O-benzoyl-5-O-(methyl sulfonyl)-1, a 2-O-isopropylidene-alpha D-glucofuranose, 1, 2, 3, 4-G O-isopropylidene-6-O -(tris RUHONIRU)- Alpha D-galactopyranose, 1, 2, 5, 6-G O-isopropylidene-3-O - (PARATORIRU sulfonyl)- Alpha D-AROFURANOSU, 1 and 2-O-isopropylidene-6-O-(PARATORIRU sulfonyl)-beta L- the id - furanose -- The 2 and 2'-G methyl -1, a 3-dioxolane-4-methanol, and the photoresist constituent according to claim 1 chosen from the group who consists of a N-O acetal with the following structure expression.

[Formula 3]



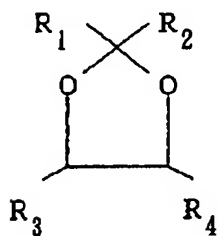
Here, n expresses the number of 1 to 15, and R10 expresses alkyl (CN H2N+1).

[Claim 13] The photoresist constituent according to claim 1 chosen from the group which a solvent becomes from propylene glycol monoalkyl ether, propylene glycol alkyl ether acetate, butyl acetate, a xylene, ethylene glycol monoethyl ether acetate, and a jig rim.

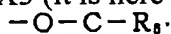
[Claim 14] The photoresist constituent according to claim 1 whose solvent is a jig rim.

[Claim 15] a) 1 - 40% of c 1 - 25% of insidious photo-oxide, and 10 - 40% [ of b film formation polymers ] organic additives with the following structure expression, and d -- the approach of forming a photoresist image on a substrate and manufacturing a semiconductor device by applying the positive type photoresist constituent which consists of mixture of a suitable solvent on a suitable substrate.

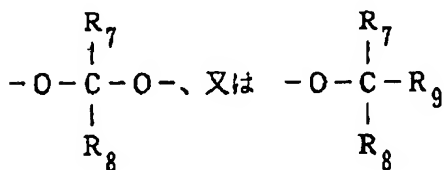
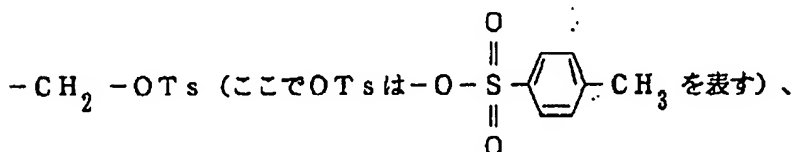
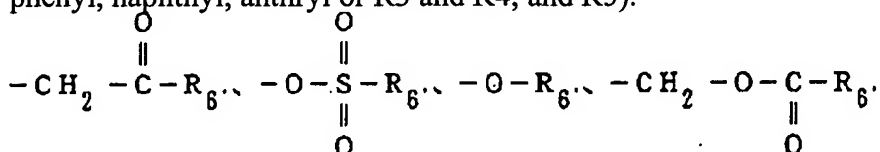
[Formula 4]



R1 is phenyl, permutation phenyl, or alkyl (CN H2N+1 and N). And R2 desirable -- 1, 2, or 3 -- expressing -- R3 And R4 alkyl (CN H2N+1), the cycloalkyl which has ten carbon atoms from four pieces preferably, -CN, -NO2, a halogen atom, -CX3 (it is here and X expresses a halogen atom), and -SO3-R5 (here -- it is -- R5 -- H, -CX3, and -PO3 -- or)



It is [Formula 5] showing (the anthryl by which R6 was permuted by one or the radical beyond it of alkyl (CN H2N+1) phenyl, naphthyl, anthryl or R3 and R4, and R5).



Here, it is R7 and R8. And R9 R3, R4, or R5 You may be one of radicals.

[Claim 16] The photoresist constituent according to claim 15 whose insidious photo-oxide is iodonium salt or sulfonium salt.

[Claim 17] The photoresist constituent according to claim 15 whose insidious photo-oxide is a phenyliodonium salt or phenyl sulfonium salt.

[Claim 18] The photoresist constituent according to claim 15 whose film formation polymer is an imide polymer or a hydroxystyrene polymer.

[Claim 19] The photoresist constituent according to claim 15 whose film formation polymer is polyimide with which about 5 to about 98% of the imide radical is blocked by the acid permutation active group.

[Claim 20] The photoresist constituent according to claim 19 whose film formation polymer is Pori (maleimide-course CHIREN).

[Claim 21] The photoresist constituent according to claim 15 whose film formation polymer is a hydroxystyrene polymer by which about 5 to about 98% of the hydroxystyrene radical is blocked by the acid permutation active group.

[Claim 22] The photoresist constituent according to claim 21 whose film formation polymer is Pori (hydroxystyrene) or Pori (hydroxystyrene-2 sulfur oxide).

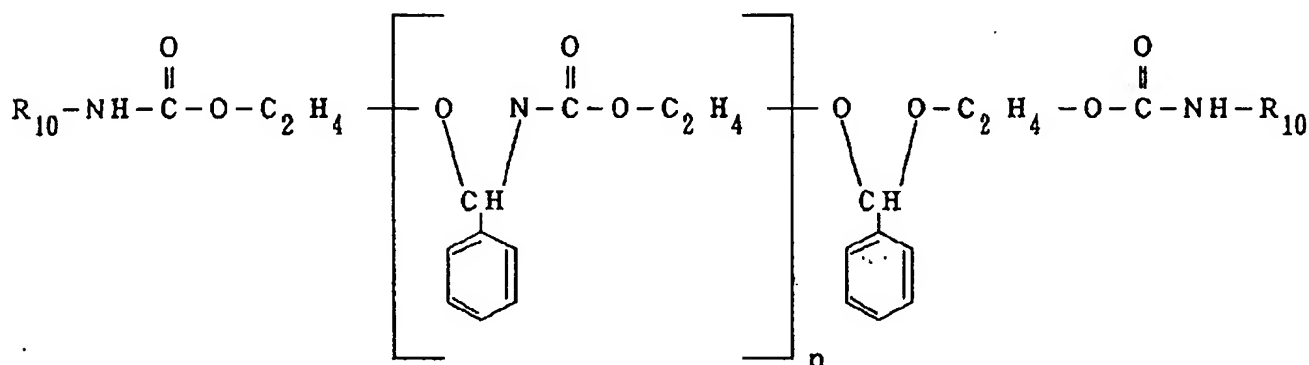
[Claim 23] The photoresist constituent according to claim 21 whose acid permutation active group is an oxy-carbonyl group.

[Claim 24] The photoresist constituent according to claim 23 whose acid permutation active group is a t-butoxycarbonyl group.

[Claim 25] The photoresist constituent according to claim 15 whose organic additive is an acetal or ketal.

[Claim 26] An organic additive 1, the 4-G O-tosyl -2, a 3-O-isopropylidene-L-sleigh toll, An oligo acetal, a diacetone-D-glucose, 3-O-acetyl-6-O-benzoyl-5-O-(methyl sulfonyl)-1, a 2-O-isopropylidene-alpha D-glucofuranose, 1, 2, 3, 4-G O-isopropylidene-6-O -(tris RUHONIRU)- Alpha D-galactopyranose, 1, 2, 5, 6-G O-isopropylidene-3-O - (PARATORIRU sulfonyl)- Alpha D-AROFURANOSU, 1 and 2-O-isopropylidene-6-O-(PARATORIRU sulfonyl)-beta L- the id - furanose -- The 2 and 2'-G methyl -1, a 3-dioxolane-4-methanol, and the photoresist constituent according to claim 15 chosen from the group who consists of a N-O acetal with the following structure expression.

[Formula 6]



Here, n expresses the number of 1 to 15, and R10 expresses alkyl (CN H2N+1).

[Claim 27] The photoresist constituent according to claim 15 chosen from the group which a solvent becomes from propylene glycol monoalkyl ether, propylene glycol alkyl ether acetate, butyl acetate, a xylene, ethylene glycol monoethyl ether acetate, and a jig rim.

[Claim 28] The photoresist constituent according to claim 15 whose solvent is a jig rim.

[Translation done.]

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a photoresist constituent useful to ultraviolet C (deep-UV) lithography or excimer laser lithography. This constituent is useful to exposure on the wavelength (248nm, 308nm) which shows high resolution, high contrast, and high sensitivity in an ultraviolet C (deep-UV) exposure band (250 to 300 nm wavelength), a medium wave length ultraviolet-rays (mid-UV) exposure band (300 to 350 nm wavelength), and the conventional ultraviolet-rays exposure band (350 to 450 nm wavelength), and is usually obtained by the source of an excimer laser, or exposure by X-ray irradiation.

[0002]

[Description of the Prior Art] A photoresist constituent is used at the micro lithography process at the time of manufacturing detailed electronic parts, such as a computer chip and an integrated circuit. At this process, the thin paint film of a photoresist constituent is first formed on a substrate ingredient like the silicon wafer usually used in case an integrated circuit is manufactured. Next, BEKU [ the substrate which gave the paint film ] in order to evaporate the solvent in a photoresist constituent and to make a paint film fix on a substrate. Then, the substrate [ BEKU / substrate ] is exposed in the shape of an image with a radiation.

[0003] The exposure section on the front face of a paint film changes with such radiation exposure chemically. Generally at current and a micro lithography process, a visible ray, ultraviolet rays (UV), an electron ray, and X-ray emission energy are used as a radiation. After exposing in the shape of an image as mentioned above, the substrate in which the paint film was formed is processed with a developer, and the radiation exposure section or the unexposed part of a paint film is dissolved and removed.

[0004] There are two types of photoresist constituents, a negative mold and a positive type. When the photoresist constituent of a negative mold is exposed in the shape of an image with a radiation, it is hard coming to dissolve the exposure section by the radiation of a resist constituent in a developer (for example, thing which crosslinking reaction produces), and, on the other hand, comparatively becomes easy to dissolve the unexposed part of a photoresist paint film to a developer. Therefore, if the resist of the negative mold after exposure is processed with a developer, the unexposed part of a photoresist paint film will be removed and a negative-mold image will be formed in a paint film. Thereby, the part of a request of the substrate to which the photoresist constituent has adhered is exposed.

[0005] On the other hand, when the photoresist constituent of a positive type is exposed in the shape of an image with a radiation, it becomes easy to dissolve the exposure section by the radiation of a photoresist constituent in a developer (for example, thing which a rearrangement reaction produces), and is comparatively hard coming to dissolve an unexposed part in a developer. Therefore, if the photoresist of the positive type after exposure is processed with a developer, the exposure section of a paint film will be removed and a positive type image will be formed in a paint film. Thereby, the part of a request of a substrate is exposed too.

[0006] Thus, after processing with a developer, the substrate from which the paint film was removed partially is processed with an etching reagent or plasma gas. The substrate of a part from which the photoresist paint film was removed by the etching reagent or plasma gas is etched. Since the substrate of a part with which the photoresist paint film remains is protected, the pattern corresponding to the photo mask used when exposing in the shape of an image with a radiation is formed on a substrate ingredient.

[0007] The residual section of a photoresist paint film is exfoliated after this, and the substrate front face etched vividly

is obtained. Since \*\*\*\*-proof to the etching reagent of the increase of an adhesive property and this layer of the photoresist layer which remains depending on the case, and the substrate in the bottom of it is increased, it is desirable after a development process to heat-treat a photoresist layer before an etching process. The resist by which current use is carried out has some faults. For example, the resist of the positive type which uses as the base the novolak resin blended using the transparent ingredient to short wavelength required to obtain [ for a limitation to be in resolution, since the resist of almost all negative molds is swollen at the time of development, and ] high resolution has very blunt sensibility like the case of the resist of the positive type which uses polymethylmethacrylate as the base.

[0008] the approach of solving these problems develops -- having had (multilayer resist) -- those approaches are complicated, and they need many routing counters in order to form a device layer. An ideal resist can be exposed by the monolayer by the exposure of ultraviolet C (200 to 300nm) (DUV), an X-ray, or an electron ray.

[0009] It is also an indispensable property for a resist with high resolution that it is high sensitivity. From an economical field, a high throughput is required in manufacture of a semiconductor device. That is, time amount required to expose each wafer must be pressed down to the minimum. Consequently, the exposure energy per unit area of a resist is controlled. Furthermore, there is what has the few total energy in the wavelength region used for exposing high resolution depending on an aligner. In this case, the energy used on a wafer front face can be reduced further.

[0010] In order to solve the problem of a throughput IBM Wilson \*\* -- The concept of "chemistry magnification" was introduced (). [ C.G.] Wilson, H.Ito, J.M.Frechet, and T.G.Tessier -- and -- F.M.Houlihan, J.Electrochem, Soc.1986, and Vol.133 (1) and 181-187 Page. In a chemistry multiplication mechanism, the protective group of a hydroxy permutation polymer or an imide permutation polymer \*\*\*\*s by the catalysis of the acid generated by light. Since the polymer protected is oleophilic, it is dissolved in a nonpolar solvent. However, the polymer by which deprotection was carried out is the matter with a very high hydrophilic property, and is dissolved in the water solution and other polar solvents of a base. Therefore, the difference of the solubility started by optical exposure is used for forming the positive or negative pattern of a mask according to the polarity of a developer. As a protective group, an ester group, a ether group, a formyl group, or a cull BONETO radical is raised. Since pyrolysis nature and composition are easy, especially t-butyl cull BONETO radical is desirable as a protective group. At a chemistry magnification process, it is the main requirements that the hydrogen combined with the carbon like alpha is effective in formation of carbonium ion. Although carbonium ion emits a proton (H+) in the BEKU phase after exposure, this elimination reaction is very important for a catalyst cycle. It is because a protective group \*\*\*\*s further with the acid by which regeneration was carried out. Each acid-content child's turnover (namely, catalyst chain length) in a practical resist compound is in the range of 800 to 1200. However, it depends for deprotection and a turnover on the baking temperature after exposure, BEKU time amount, and the approach of BEKU greatly.

[0011] After the metal lift-off method forms a pattern in a positive resist first, it is used for forming a metaled thin line on a front face by making a metal vapor-deposit on this pattern. A solvent removes a photoresist film and it leaves a desired metal wire on the substrate of a basis. However, a photoresist cannot be dissolved if the wall of a pattern is covered with a metal. Therefore, the approach of forming the cross section of a form which prevents covering the wall of a pattern with a metal was developed. From the above-mentioned viewpoint, it must stretch and come out of the upper part of a photoresist film on the wall so that a wall may be interrupted from the metal vapor-deposited from a top.

[0012] The cross-section form of such a T character mold or an overhang mold does not usually become a problem to have suited manufacturing a semiconductor device by approaches other than the metal lift-off method. However, by the protection polymer system used for an ironical thing at the chemistry amplifying method in ultraviolet C lithography, this T character mold cross section is a typical problem. Careful attention must be paid and the contamination which exists in an environment like a base must be removed. The base which is floating in the usual manufacture environment neutralizes the acid generated by the light which exists in the front face of the exposed wafer (before BEKU after exposure), and prevents the deprotection reaction which occurs in the BEKU phase after exposure. Thereby, the front face of a wafer becomes [ being protected with as, and ], and acts as the development in process in an alkali water solution, and a surface coat.

[0013] The photoresist constituent under the surface coat of the exposure section is dissolved into development after exposure by the chemical rays or laser of suitable wavelength. Moreover, the surface coat of the exposure section secedes from an unexposed part. Since the rate which the resist of the exposure section dissolves is very earlier than the rate at which a surface coat secedes from an unexposed part consequently, a cross-section form becomes a T character

mold. If the worst happens, into development, the surface coat of the exposure section may not secede from an unexposed part, but may form a slot. This is what happens ordinarily on an ultraviolet C photoresist compound, especially submicron level.

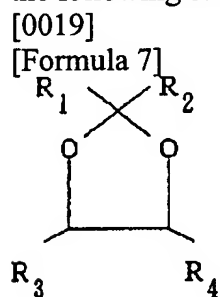
[0014] In manufacture of the semiconductor device using a photoresist, the cross-section form of a T character mold has a bad influence on forming an exact pattern vividly on a semi-conductor substrate. This T character type of cross-section form serves as hindrance at the time of forming a lithograph image with a clear perpendicular wall, and an image with especially the resolution of less than 1.0 microns.

[0015] The base which is floating in the air which neutralizes the acid generated by the light on a resist front face is generated by various matter usually used. An object like the new coating with which the contamination in an environment very like the volatile amine of a minute amount was applied to the wall of a laboratory can serve as a generation source. By storing and processing the wafer which applied the photoresist in the air purified through the efficient carbon filter, it is [ the effect of such a contamination ] minimum-hard, and it can be stopped. As other solution approaches, in order to isolate a photoresist front face from the contamination in such an environment, there is the approach of using protective film material. However, in order to enforce these approaches, the addition of a processing process or a raw material is needed, and the Hiroshi book must be thrown in. In order to make ultraviolet C lithography into practical manufacture means, such as a semiconductor device, the simple solution approach is required.

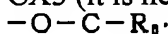
[0016] [Problem(s) to be Solved by the Invention] This invention relates to ultraviolet rays and the positive type photoresist which can be especially exposed by the ultraviolet rays of a 200 to 350nm wavelength region, without forming the cross section of the T character mold which shows quantity KONRASUTO, high sensitivity, and high resolution by multicomponent, and poses a problem by the positive type ultraviolet C photoresist. From such a photoresist, the film with which it had the improved adhesive strength, solubility, and relief resistance, and formation of a pit decreased substantially is formed.

[0017] In the polymer system protected by the t-butoxycarbonyl (t-boc) used for an ultraviolet C photoresist, it can be said that formation of the cross section of a slot or a T character mold is characteristic. Formation of the surface coat used as the cause which forms a T character mold cross section is considered to be the result of the interaction of the above-mentioned polymer system and the contamination which is floating in air. The formed surface coat is meltable to the aqueous developer of a base. In order to process a wafer in the interior of a room which purified the air of a clean room with the filter further or to isolate and protect a photoresist film from a perimeter, preparing a protective coating layer is proposed until now.

[0018] [Means for Solving the Problem] This invention offers the very simple solution approach to the above-mentioned problem by specifying the class of organic additive added into a photoresist constituent. These organic additives have the following structure expression.



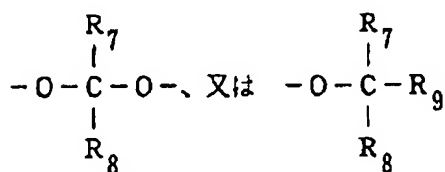
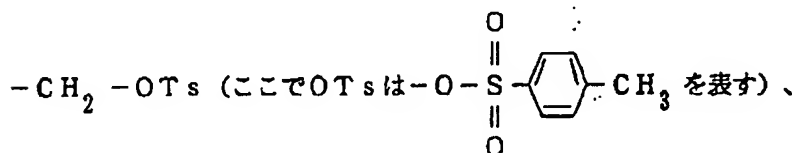
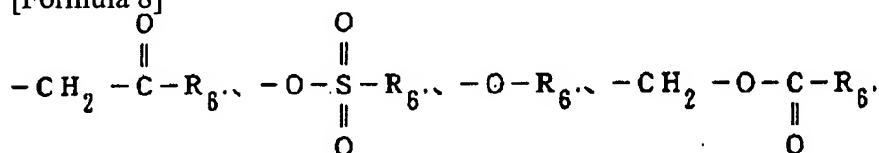
Here, R1 is phenyl, permutation phenyl, or alkyl (CN H<sub>2</sub>N+1 and N). And R2 desirable -- 1, 2, or 3 -- expressing -- R3 And R4 alkyl (CN H<sub>2</sub>N+1), the cycloalkyl which has ten carbon atoms from four pieces preferably, -CN, -NO<sub>2</sub>, a halogen atom, -CX<sub>3</sub> (it is here and X expresses a halogen atom), and -SO<sub>3</sub>-R<sub>5</sub> (here -- it is -- R<sub>5</sub> -- H, -CX<sub>3</sub>, and -PO<sub>3</sub>



-- or)

It is [0020] showing (the anthryl by which R6 was permuted by one or the radical beyond it of alkyl (CN H2N+1) phenyl, naphthyl, anthryl or R3 and R4, and R5).

[Formula 8]

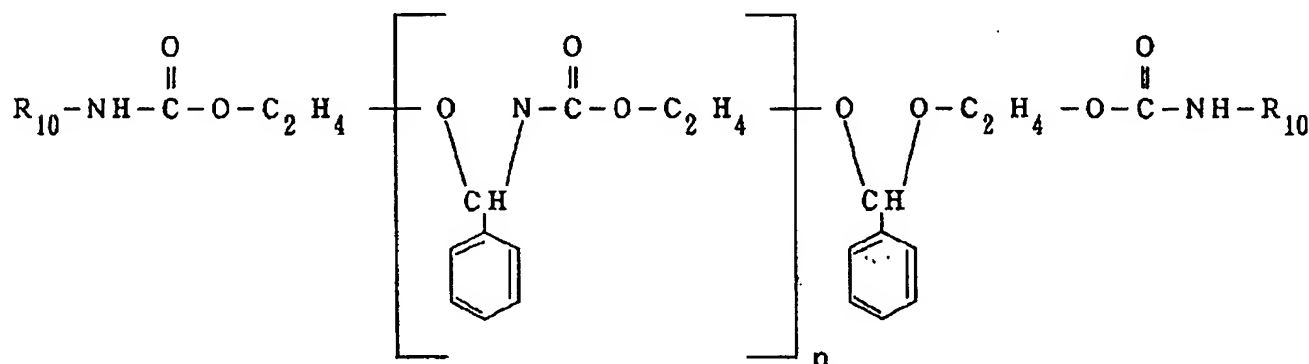


Here, it is R7 and R8. And R9 R3, R4, or R5 You may be one of radicals. R3 And R4 You may be a part of cyclic structure expressed with  $-(\text{CR}')_N-$  (it is here, N expresses the number of 1 to 8, and R' expresses the radical of either H or R3, R4 or R5).

[0021] An organic additive is a desirable acetal like a 1, 4-G O-tosyl -2, 3-O-isopropylidene-L-sleigh toll oligo. acetal, diacetone-D-glucose or 3-O-acetyl-6-O-benzoyl-5-O-(methyl sulfonyl)-1, and 2-O-isopropylidene-alpha D-glucofuranose, or a ketal derivative. As other desirable additives, it is 1, 2, 3, and 4-G O-isopropylidene-6-O. -(tris RUHONIRU)- Alpha D-galactopyranose, 1, 2, 5, 6-G O-isopropylidene-3-O -(PARATORIRU sulfonyl)- Alpha D-AROFURANOSU, 1 and 2-O-isopropylidene-6-O-(PARATORIRU sulfonyl)-beta L- the id -- the - furanose, 2, and 2'-G methyl -1, a 3-dioxolane-4-methanol, a N-O acetal with the following structure expression, etc. are raised.

[0022]

[Formula 9]



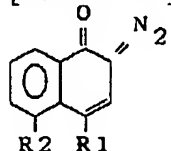
Here, n expresses the number of 1 to 15, and R10 expresses alkyl (CN H2N+1). As for a photoresist compound, it is desirable that a protection polymer (for example, polymer protected by t-boc or other protective groups) like



polystyrene (t-butoxycarbonyl) maleimide, Pori (t-butoxy cull BONIRUHIDOROKISHI styrene), or Pori (t-butoxycarbonyl-hydroxystyrene-2 sulfur oxide) is included. Furthermore, as for this compound, it is desirable that an organic or inorganic photo-oxide generating agent is also included.

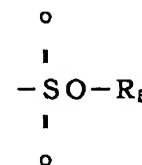
[0023] Insidious photo-oxide is a diazo naphthoquinone [0024].

[Formula 10]



\*\* -- diazoketone [ like ], valeraldehyde, or [0025]

[Formula 11]



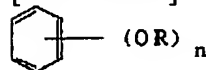
\*\* -- a 5-diazo valeraldehyde derivative [ like ] (here -- R1 and R2)

It comes out, a part of sulfonyl group expressed or H (however, it is not the same) is expressed, and it is R3 and R4. And R5 It is chosen out of various matter with which generating an acid by the exposure of the light [ like ] showing an alkyl group or an aryl group is known. Furthermore, in this invention, onium salt like diazonium salt, iodonium salt, or sulfonium salt may be used as photo-oxide. For example, R6 N2+Y-, 2 (R6) I+Y-, 3 (R6) S+Y - Here, it is R6. Phenyl or permutation aryl is expressed. Y which is a counter ion - It is chosen from the anion covering the large range. However, if the potential danger for the marginal stability of an onium bisulfate or a chloride salt and the binding property of the manufactured circuit which an arsenic, Lynn, boron, or antimony has is considered, for example HSO4-, Cl-, BF4-, PF6-, and AsF6-, Or SbF6 - An anion [ like ] Truffe RATO (CF3 SO3-), Compared with methanesulfonate or an anion like general RSO3- (R expresses alkyl, aryl, permutation alkyl, or permutation aryl here), it cannot be said that it is not much suitable. However, since it is the conjugate base of strong acid, it sets to the following balance, and this counter ion is H+. + Y- = In case the proton generated by exposure of HY onium salt and the reaction following it generates HY, it is not consumed, but it remains so that an acid permutation activity protective group can be attacked. This is the main properties of this counter ion.

[0026] As desirable insidious photo-oxide, organic [ which is expressed with diphenyliodonium truffe RATO, triphenylsulfonium hexafluoroantimonate, diphenyliodonium hexafluorophosphate, phenyl acyl sulfonium hexafluoroantimonate, and the following structure expression / other / PAG ] is raised.

[0027]

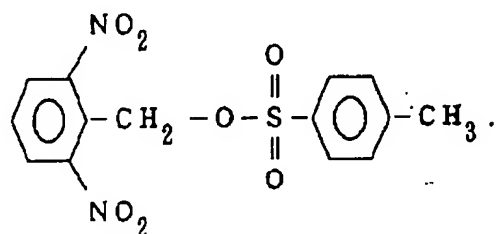
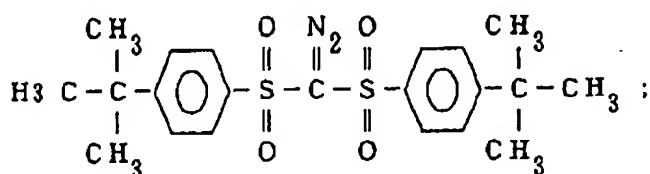
[Formula 12]



Here, n expresses the number of 1 to 4, and, as for R, -SO2-CX3-SO2-CH3 and X express a halogen.

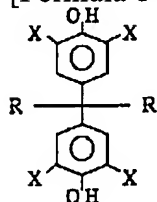
[0028]

[Formula 13]



[0029]

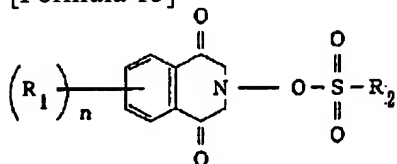
[Formula 14]



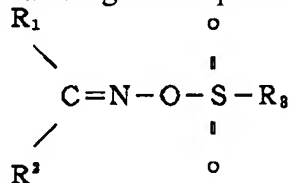
Here, R expresses an alkyl group ( $\text{C}_n\text{H}_{2n+1}$ ,  $n=1-3$ ) or H, and X expresses a halogen.

[0030]

[Formula 15]



Here, it is R1. NO<sub>2</sub>, -CN, or a halogen is expressed and it is R2. CX<sub>3</sub> or (X is a halogen) an alkyl group ( $\text{C}_n\text{H}_{2n+1}$ ,  $n=$

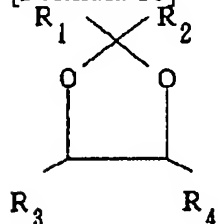


1-2) is expressed.

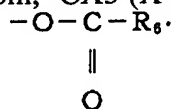
here -- R1 And R2 an alkyl group ( $\text{C}_n\text{H}_{2n+1}$ ) -- expressing -- at least one -H - it permutes by CN, NO<sub>2</sub>, the halogen, or a part of \*\*\*\*\* . R3 CX<sub>3</sub> or (X= halogen) H is expressed. this invention -- 1 - 40% of c 1 - 25% of a insidiousness photo-oxide, and 10 - 40% [ of b film formation polymers ] organic additives with the following structure expression, and d -- the positive type photoresist constituent which consists of mixture of a suitable solvent is offered.

[0031]

[Formula 16]

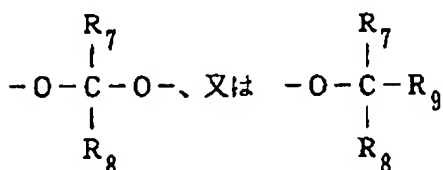
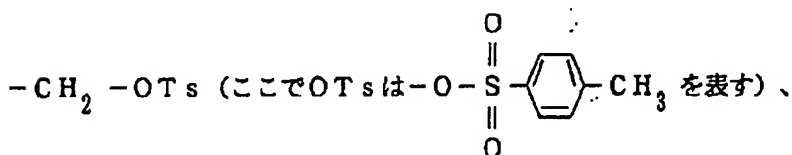
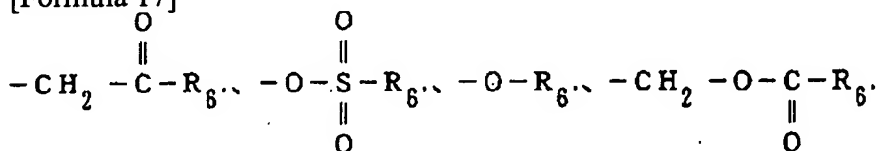


Here, it is R1. And R2 Phenyl, permutation phenyl, or alkyl (CN H2N+1 and N are 1, 2, or 3 preferably) is expressed. R3 And R4 Alkyl (CN H2N+1), cycloalkyl which has ten carbon atoms from four pieces preferably, -CN, -NO2, a halogen atom, -CX3 (X expresses a halogen atom here), and -SO3-R5 (here -- R5 -- H, -CX3, and -PO3 -- or)



It is [0032] showing (the anthryl by which R6 was permuted by one or the radical beyond it of alkyl (CN H2N+1) phenyl, naphthyl, anthryl or R3, R4, and R5).

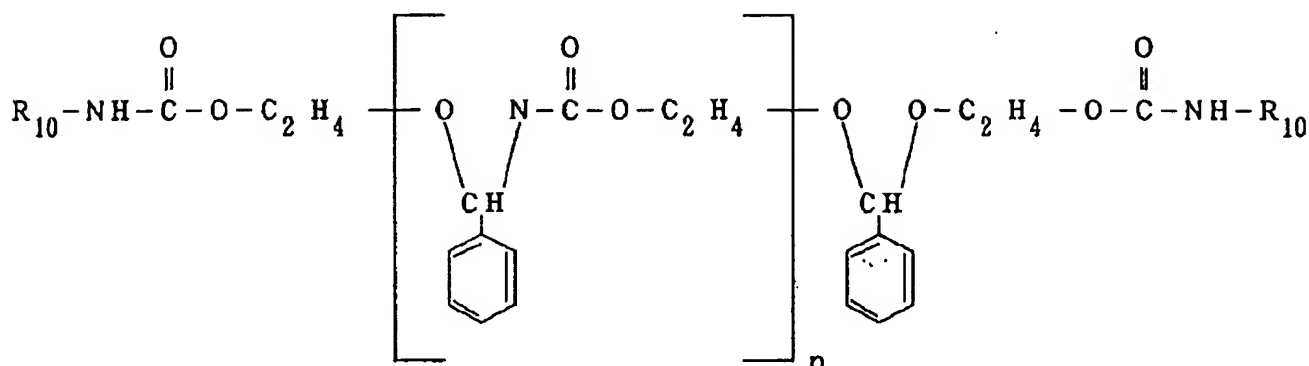
[Formula 17]



Here, it is R7 and R8. And R9 R3, R4, or R5 As insidious photo-oxide, iodonium salt or sulfonium salt is desirable, and a phenyliodonium salt or phenyl sulfonium salt is [ that it is easy to be one of radicals ] the most desirable. As a film formation polymer, an imide polymer or a hydroxystyrene polymer is desirable. As polyimide, that from which about 5 to about 98% of the imide radical in a polymer is protected by the acid permutation active group is desirable. But a desirable film formation polymer is Pori (maleimide-course CHIREN). As a hydroxystyrene polymer, that from which about 5 to about 98% of the hydroxystyrene radical in a polymer is protected by the acid permutation active group is desirable. But a desirable hydroxystyrene polymer is Pori (hydroxystyrene) or Pori (hydroxystyrene-2 sulfur oxide). [0033] As an acid permutation active group, an oxy-carbonyl group is desirable, and a t-butoxycarbonyl group is the most desirable. As an organic additive, an acetal or ketal is desirable and the compound chosen from the group who consists of a 1, 4-G O-tosyl -2, 3-O-isopropylidene-L-sleigh toll, oligo acetal, diacetone-D-glucose and 3-O-acetyl-6-O-benzoyl-5-O-(methyl sulfonyl)-1, and 2-O-isopropylidene-alpha D-glucofuranose is the most desirable. As other desirable additives, it is 1, 2, 3, and 4-G O-isopropylidene-6-O. -(tris RUHONIRU)- Alpha D-galactopyranose, 1, 2, 5, 6-G O-isopropylidene-3-O -(PARATORIRU sulfonyl)- Alpha D-AROFURANOSU, 1 and 2-O-isopropylidene-6-O-(PARATORIRU sulfonyl)-beta L- the id -- the - furanose, 2, and 2'-G methyl -1, a 3-dioxolane-4-methanol, a N-O acetal with the following structure expression, etc. are raised.

[0034]

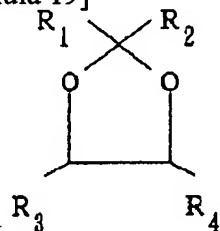
[Formula 18]



Here, n expresses the number of 1 to 15, and R10 expresses alkyl (CN H2N+1). moreover, this invention -- 1 - 40% of c 1 - 25% of a insidiousness photo-oxide, and 10 - 40% [ of b film formation polymers ] organic additives with the following structure expression, and d -- the approach of forming a photoresist image on a substrate and manufacturing a semiconductor device is offered by applying the positive type photoresist constituent which consists of mixture of a suitable solvent on a suitable substrate.

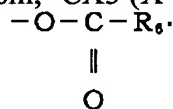
[0035]

[Formula 19]



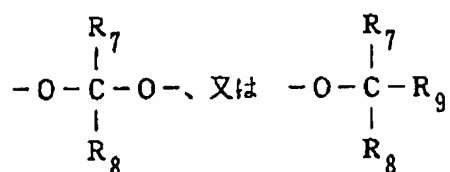
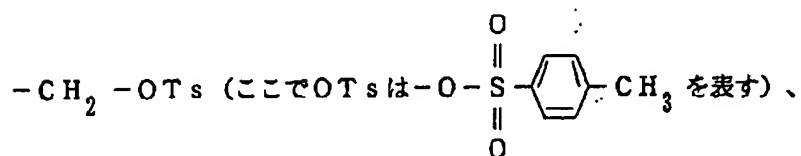
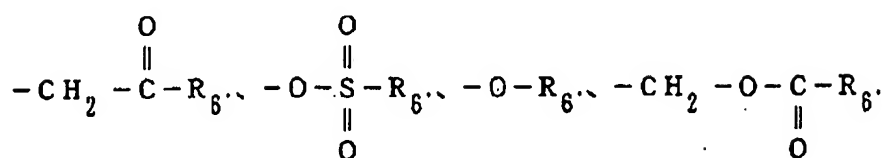
【化2】 【化5】 【化8】 【化17】 【化

Here, it is R1. And R2 Phenyl, permutation phenyl, or alkyl (CN H2N+1 and N are 1, 2, or 3 preferably) is expressed. R3 And R4 Alkyl (CN H2N+1), cycloalkyl which has ten carbon atoms from four pieces preferably, - CN, -NO2, a halogen atom, -CX3 (X expresses a halogen atom here), and -SO3-R5 (here -- R5 -- H, -CX3, and -PO3 -- or)



It is [0036] showing (the anthryl by which R6 was permuted by one or the radical beyond it of alkyl (CN H2N+1) phenyl, naphthyl, anthryl or R3, R4, and R5).

[Formula 20]



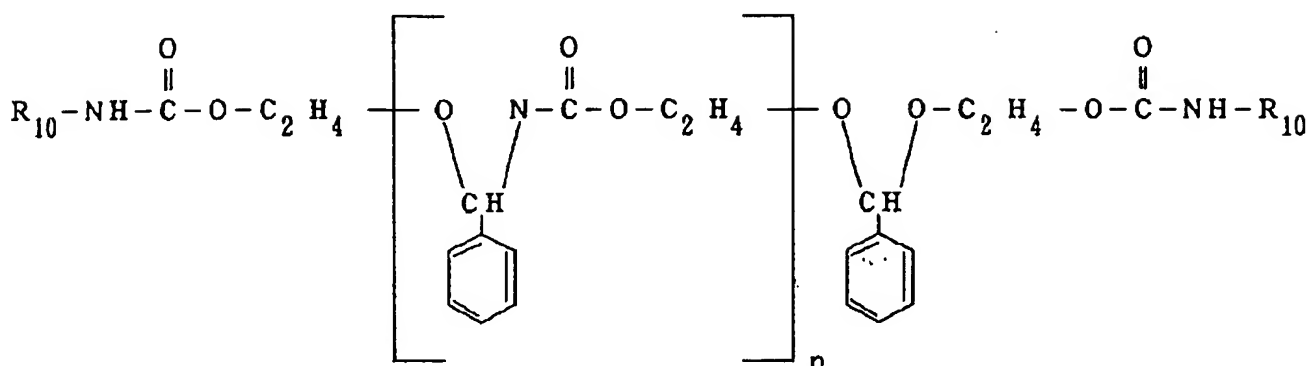
Here, it is R7 and R8. And R9 R3, R4, or R5 It is desirable to heat-treat the substrate which expresses that it is easy to be one of radicals and which applied the photoresist, and to remove a solvent completely substantially. An aqueous alkali developer removes the constituent of the part which exposed the photoresist constituent in the shape of an image, and was exposed in the shape of an image. BEKU [ just before this removal process or immediately after / a substrate ].

[0037] As insidious photo-oxide, iodonium salt or sulfonium salt is desirable, and a phenyliodonium salt or phenyl sulfonium salt is the most desirable. As a film formation polymer, an imide polymer or a hydroxystyrene polymer is desirable. As polyimide, that from which about 5 to about 98% of the imide radical in a polymer is protected by the acid permutation active group is desirable. But a desirable film formation polymer is Pori (maleimide-course CHIREN). As a hydroxystyrene polymer, that from which about 5 to about 98% of the hydroxystyrene radical in a polymer is protected by the acid permutation active group is desirable. But a desirable hydroxystyrene polymer is Pori (hydroxystyrene) or Pori (hydroxystyrene-2 sulfur oxide).

[0038] As an acid permutation active group, an oxy-carbonyl group is desirable, and a t-butoxycarbonyl group is the most desirable. As an organic additive, an acetal or ketal is desirable and the compound chosen from the group who consists of a 1, 4-G O-tosyl -2, 3-O-isopropylidene-L-sleigh toll, oligo acetal, diacetone-D-glucose and 3-O-acetyl-6-O-benzoyl-5-O-(methyl sulfonyl)-1, and 2-O-isopropylidene-alpha D-glucofuranose is the most desirable. As other desirable additives, it is 1, 2, 3, and 4-G O-isopropylidene-6-O. -(tris RUHONIRU)- Alpha D-galactopyranose, 1, 2, 5, 6-G O-isopropylidene-3-O -(PARATORIRU sulfonyl)- Alpha D-AROFURANOSU, 1 and 2-O-isopropylidene-6-O-(PARATORIRU sulfonyl)-beta L- the id -- the - furanose, 2, and 2'-G methyl -1, a 3-dioxolane-4-methanol, a N-O acetal with the following structure expression, etc. are raised.

[0039]

[Formula 21]



Here, n expresses the number of 1 to 15, and R10 expresses alkyl (CN H2N+1).

[0040] A photoresist constituent is obtained by mixing the above-mentioned component in a suitable solvent. In a desirable mode, the amount of the film formation polymer in a photoresist is about 20% to about 30% still more preferably about 40% preferably from 10% of the weight of a formed element, i.e., the weight of the component of photoresist constituents other than a solvent. In a desirable mode, the amount of the insidious photo-oxide in the photoresist of this invention is about 8% to about 20% most preferably about 25% in about 1% of the weight of the formed element of a photoresist constituent. The amount of the organic additive in a resist is about 3% to about 15% most preferably about 25% in about 1% of the weight of the formed element of a photoresist constituent. A photoresist constituent is obtained propylene glycol monoalkyl ether, propylene glycol alkyl ether acetate, butyl acetate, a xylene, a solvent like ethylene glycol monoethyl ether acetate, and by mixing with a jig rim most preferably in insidious photo-oxide, an above-mentioned film formation polymer, and an above-mentioned organic additive. 30 to about 95% of the weight of the formed element of a photoresist constituent is desirable the most desirable, and the amount of a solvent is about 50% to about 75%.

[0041] Before applying the above-mentioned resin, a sensitizer, and the mixed solution of a solvent to a substrate, a surfactant still like a coloring agent, a color, a vertical line formation inhibitor, a \*\* exhibition agent, a plasticizer, an adhesion promoter, an accelerating agent, a solvent, and the Nonion system surfactant may be added if needed in this solution. As an example of the color which can be used for the photoresist constituent of this invention, Methyl Violet 2B (C. I.No.42535), a crystal violet (C. I.No.42555), Malachite Green (C. I.No.42000), Victoria blue B (C. I.No.44045), neutral red (C. I.No.50040), etc. are raised. The amount of the color which can be used is 1 to 10% of level of the sum total weight of resin and a sensitizer. If such a color is used, since the backscattering of the light in a substrate can be prevented, resolution can be raised.

[0042] A vertical line formation inhibitor can be used to about 5% of level of the sum total weight of insidious photo-oxide, a film formation polymer, and an organic additive. As an usable plasticizer, phosphoric-acid Tori (beta-chloroethyl) ester, a JIKAN fur, polypropylene, acetal resin, phenoxy resin, alkyl resin, etc. are raised. The amount of the plasticizer which can be used is about 1 to 10% of level of the sum total weight of resin and a sensitizer. If such a plasticizer is used, the coating nature of a constituent can improve and the film of smooth and uniform thickness can be formed on a substrate.

[0043] As an usable adhesion promoter, beta (3, 4-epoxycyclohexyl)-ethyltrimethoxysilane and p-methyl-disilane-methyl methacrylate, vinyl trichlorosilane, gamma-aminopropyl triethoxysilane, etc. are raised. Such an adhesion promoter can be used to about 4% of level of the sum total weight of insidious photo-oxide, a film formation polymer, and an organic additive.

[0044] A solvent can be used to 95% of the weight of the formed element in a constituent. After applying a photoresist solution on a substrate with a natural thing and drying, a solvent is removed completely substantially. As an Nonion system surface active agent which can be used, nonyl phenoxy poly (ethyleneoxy) ethanol, octyl phenoxyethanol, etc. are raised. Such an Nonion system surfactant can be used to about 10% of level of the sum total weight of insidious photo-oxide, a film formation polymer, and an organic additive.

[0045] Thus, the obtained photoresist solution is applied to a substrate by approaches used from the former in the

photoresist technique, such as dip coating, a spray coating method, a rotation method, and a spin coating method. For example, when applying with a spin coating method, in order to obtain the paint film of desired thickness, the percentage of a formed element is adjusted and it decides on the type of the equipment to be used, and the time amount of a spin process. as a thing suitable as a substrate ingredient -- the [ silicon, aluminum, macromolecule resin, a silicon dioxide, the doped silicon dioxide, silicon nitride, a tantalum, copper, polish recon, the ceramics, the mixture of aluminum and copper, gallium arsenide, and ] -- the compound of an III group and the Vth group etc. is raised.

[0046] The photoresist paint film formed by the above-mentioned approach is suitable for especially the heat growth wafer that applied the silicon/silicon dioxide which is used for manufacture of a microprocessor or other detailed components for integrated circuits. It can use also for aluminum / aluminum-oxide wafer. A substrate may also contain various macromolecule resin, especially a transparent polymer like polyester. Moreover, a substrate may contain the adhesion promotion layer which consists of a suitable constituent like hexa alkyl disilazane.

[0047] After applying a photoresist solution to a substrate, a substrate is heat-treated for about 15 minutes to about 90 minutes on a hot plate in about 30 seconds to about 180 seconds, or in heat convection oven at the temperature of about 70 to about 110 degrees C. This heat treatment is performed on the conditions on which the concentration of the residual solvent in a photoresist can be reduced, without producing the pyrolysis of a sensitizer substantially. Although what is necessary is just to press down the concentration of a solvent generally to the minimum, the above-mentioned heat treatment is performed until a solvent evaporates completely substantially. Consequently, the paint film of the thin photoresist constituent of the order whose thickness is 1 micron is formed on a substrate. In a desirable mode, the temperature of heat treatment is about 85 degrees C to about 95 degrees C. Heat treatment is continued until the change rate of solvent removal becomes very small. The temperature and time amount of heat treatment are determined by the engine performance of the photoresist which a user demands, the equipment to be used, and spreading time amount required when actually manufacturing. Next, chemical rays, for example, ultraviolet rays with a wavelength of about 300 to about 450nm, an X-ray, an electron ray, an ion beam, or a laser beam is used, and the substrate which applied the photoresist is exposed in the shape of [ which was formed by the suitable mask, the negative, the stencil, the template, etc. / desired ] a pattern.

[0048] As long as a photoresist is required, it may perform the second BEKU or heat treatment before development or to the back. The range of about 120 degrees C of whenever [ stoving temperature ] is about 100 degrees C to about 110 degrees C preferably from about 90 degrees C. Heating is performed from about 30 seconds on a hot plate, and is preferably performed for about 30 minutes to about 45 minutes for about 2 minutes in about 60 seconds to about 90 seconds, or in heat convection oven.

[0049] The exposed photoresist spreading substrate is developed by removing the part which was immersed into the alkaline developer and exposed in the shape of an image. As for a developer, it is desirable to blow and stir nitrogen. The substrate is dipped into the developer until a photoresist paint film all dissolves substantially from the exposure section. As a developer, the water solution of ammonium or an alkali-metal hydroxide is raised. Tetramethylammonium hydroxide is raised as a desirable example of a hydroxide. After picking out a wafer from a developer, in order to raise the adhesive property over the substrate of a paint film and to raise the chemical stability to an etching reagent or other matter, as long as it is required, heat treatment or BEKU may be performed. In heat treatment after such development, the approach, BEKU [ a paint film and a substrate ] in the oven of the temperature below the softening temperature of a paint film, can be taken.

[0050]

[Example] Below, it has the following concrete example and the manufacture approach of the constituent of this invention and the usage are explained in detail. However, these examples do not limit the range of this invention at all, and do not show the range of the absolute conditions which hit carrying out this invention, or a value, either.

<Example 1> Jig rim 625ml was put in as 75.0g (it purchases from Aldrich) (0.772 mols) of maleimide, 80.47g (it purchases from Fisher) (0.772 mols) of styrene, and a solvent into the synthetic suspension mold stirrer of Pori (styrene-comber REIMIDO), the thermometer, and the 1l. flask with a jacket equipped with the condensator. This reaction mixture was heated to 35 degrees C, and 5.00ml of dodecane thiols was added. After purging a reaction mixture with nitrogen, 0.500g (azobisisobutironitoriru) of azo-isobutyro-dinitrile was added as a polymerization initiator. The reaction mixture was heated at 60 degrees C, and it maintained at the temperature for 2 hours. 500 moremg of azobisisobutironitoriru was added and the reaction mixture was stirred at 60 degrees C for 10 hours.

[0051] After cooling this reaction mixture to 15 degrees C, when pouring into the 5l. methanol, settlings arose. After

stirring for 15 minutes, mixture was filtered and the 2.5l. methanol washed the obtained rough product.

[0052] This rough product was remelted to 500ml THF. This solution was filtered through F-3 pad, and it washed by 100ml THF. Then, the solution was poured out into the 5l. methanol. The polymer which deposited by this was carried out the \*\* exception, and 2l. another methanol washed. Thus, the refined polymer was dried.

THF800ml was put in as 80.0g (styrene-comber REIMIDO) (1:1) (0.4 mols) of Pori, and a solvent into the 2l. flask with a jacket equipped with the synthetic suspension mold stirrer, thermometer, and nitrogen gas inlet of <example 2> N (t-butyl carbonyl) Pori (styrene-comber REIMIDO). It stirred for about 45 minutes at the room temperature, and the polymer was dissolved. This solution was cooled to -7 degrees C in the ice-acetone mixing bath. It added into the reaction mixture, stirring 54.0g (DMAP) (0.48 mols) of dimethylamino pyridines. At this time, 102.0g (G t-butyl cull BONETO) (0.467 mols) of N was added to the reaction mixture, keeping temperature at 5 degrees C. The ice bath was removed and the reaction mixture was heated at 30 degrees C for 8 hours.

[0053] 4l. of deionized water, 4l. of methanols, and 52.8g of glacial acetic acids were put in into the battery case. The reaction mixture (yellow thru/or brown) was put into the dropping funnel. The suspension mold stirrer was used for stirring of a solution. The reaction mixture was gradually added over 1 hour into deionized water-methanol mixed liquor. Since detailed yellowish brown settlings were obtained when stirred for about 2 hours, after making a supernatant flow out over 30 minutes, it carried out the \*\* exception. Thus, the obtained detailed polymer was washed by 16l. deionized water. The refined polymer was dried in the vacuum overnight and, still more finally it dried by the 60-degree C vacuum dryer.

[0054] Thus, the property of the obtained polymer is as follows.

MW = 15-25,000Mn = 10-12,000D = 1.43Tg = Permeability to 246-degree-C wavelength of 248 nm = Rate of capping by 59%t-boc = 98% <an example 3> An additive 2.6g (styrene-comber REIMIDO) of N (t-boc) Pori of the photosensitive compound solid-state which is not included and 0.43g of diphenyliodonium truffle RATO were dissolved stirring at a room temperature to 7.4g of jig rims. This solution was filtered with the 0.2-micron PTFE filter. On the silicon wafer which processed the filtered solution by hexamethyldisilazane (HMDS) beforehand, it applied so that it might become the thickness of about 1 micron. After BEKU [ this wafer ] for 60 seconds on a 90-degree C hot plate, light with a wavelength of 248nm was exposed through the mask of submicron resolution. After BEKU [ the exposed wafer ] for 60 seconds on a 110 more-degree C hot plate, negatives were developed with the alkali-metal ion free developer (AZ312MIF, product made from Hoechst Celanese Corporation), and submicron resolution was obtained. However, it turned out that an overhang cross section exists between the Rhine-tooth spaces (1-/s) of submicron level with a SEM photograph.

<Example 4> 2.6g (styrene-comber REIMIDO) of N (t-boc) Pori of the photosensitive compound solid-state containing an additive, 0.43g of diphenyliodonium truffle RATO, 1, the 4-G o-tosyl -2, and 0.22g of 3-o-isopropylidene-L-sleigh tolls were dissolved in 7.4g of jig rims. This solution was filtered with the 0.2-micron Teflon filter. The filtered solution was applied so that it might become the thickness of about 1 micron with a spin coat method on a silicon wafer. This wafer, the solvent was removed, and it exposed in the shape of an image using the light source with a wavelength of 248nm. [ on the 90-degree C hot plate ] [ for 60 seconds ] After BEKU [ the exposed wafer ] for 60 seconds on a 110-degree C hot plate, negatives were developed for 120 seconds with the metal ion free developer (0.075Ns), and submicron resolution was obtained. The SEM photograph showed that any overhang cross sections did not exist between the Rhine-tooth spaces.

<Example 5> 7.9g (styrene-comber REIMIDO) of N (t-boc) Pori, 1.303g of triphenylsulfonium hexafluoroantimonate, and 0.33g of diacetone glucoses of the photosensitive compound solid-state containing an additive were dissolved in 22.46g of jig rims. This solution was filtered with the 0.2-micron Teflon filter. The filtered solution was applied so that it might become the thickness of about 1 micron with a spin coat method on a silicon wafer. This wafer, the solvent was removed, and the uniform film was formed. [ on the 90-degree C hot plate ] [ for 60 seconds ] Then, BEKU [ the wafer which exposed the wafer in the shape of an image, and exposed it using the light source with a wavelength of 248nm ] for 60 seconds on the 110-degree C hot plate again. When the wafer was developed with the metal ion free developer, the positive type image which has submicron resolution by the exposure section was formed. The SEM photograph showed that any overhang cross sections did not exist between the Rhine-tooth spaces even if it is submicron order.

<Example 6> 5.2g (styrene-comber REIMIDO) of N (t-boc) Pori of the photosensitive compound solid-state containing an additive, 0.858g of diphenyliodonium truffle RATO, and 0.442g of N-O oligo acetals were dissolved in 14.8g of jig



rims. This solution was filtered with the 0.2-micron Teflon filter. The filtered solution was applied so that it might become the thickness of about 1 micron with a spin coat method on a silicon wafer. This wafer, and the solvent was removed. [ on the 90-degree C hot plate ] [ for 60 seconds ] BEKU [ the wafer which exposed the wafer in the shape of an image, and exposed it using the light source with a wavelength of 248nm after that ] for 60 seconds on the 110-degree C hot plate. Between BEKU after exposure and exposure, 30 minutes or more than it is sufficient from 1 minute. By developing the wafer [ BEKU / wafer / after exposure ] with an MIF developer, and removing the exposure section, the positive type image without the resist remainder with submicron resolution was formed, without forming any overhang cross sections or a T character cross section.

<Example 7> 5.2g (hydroxystyrene) of Pori of the solid-state (19% of rates of protection) protected by photosensitive compound t-boc which does not contain an additive, and 0.858g of diphenyliodonium truffle RATO were dissolved in 14.8g of jig rims. This solution was filtered with the Teflon filter. The filtered solution was applied so that it might become the thickness of about 1 micron with a spin coat method on a silicon wafer (finishing [ spreading of HMDS ]). This wafer, and the solvent was removed. [ on the 90-degree C hot plate ] [ for 60 seconds ] BEKU [ the wafer was exposed in the shape of an image using the light source with a wavelength of 248nm after that, and / this ] for 60 seconds on the 110 more-degree C hot plate. When negatives were developed with the MIF developer, it turned out that a film loses touch with a SEM photograph considerably since adhesion is insufficient, and the pit is formed. Even when line breadth was large, high 1/s resolution was not obtained.

<Example 8> 5.2g (hydroxystyrene) of Pori of the solid-state (19% of rates of protection) protected by photosensitive compound t-boc containing an additive, 0.858g of diphenyliodonium truffle RATO, 1, the 4-G o-tosyl -2, and 0.442g of 3-o-isopropylidene sleigh tolls were dissolved in 14.8g of jig rims. This solution was filtered with the Teflon filter. The filtered solution was applied so that it might become the thickness of about 1 micron with a spin coat method on a silicon wafer (finishing [ processing by HMDS ]). This wafer, and it exposed in the shape of an image using the light source with a wavelength of 248nm. [ on the 90-degree C hot plate ] [ for 60 seconds ] After BEKU [ the exposed wafer ] for 60 seconds on a 110 more-degree C hot plate, the exposure part was developed with the MIF developer (0.075Ns), and the lithograph image was obtained. It was checked that the adhesive property of the film at the time of adding an additive is improving very much compared with the case where an additive is not added. moreover, it turned out that it is markedly alike and can improve by adding an additive also about the relief of a film, or formation of a pit.

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[Translation done.]